

## Compositional and temperature dependent electrical behaviour of zinc- substituted copper- ferri-chromates

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**Abstract** . The compositional and thermal variation of electrical properties of  $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$  ( $x = 0.0, 0.2, 0.4, 0.6$ ) spinel ferrite system were studied by means of d.c. resistivity and thermoelectric power measurements. The electrical parameters like Fermi - energy charge carrier concentration and mobility were determined and probable conduction mechanism in the system has been suggested.

**Keywords** Ferrites, electrical properties, conduction mechanism.

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### 1. Introduction

The study of transition metal oxide particularly spinel ferrites is of great importance from both fundamental and applied research points of view.

Ferrites have a very high resistivity, which is one of the considerations for microwave applications. The order of magnitude of the resistivity greatly influences the dielectric and magnetic behavior of ferrites. This has aroused considerable interest in the electrical properties of ferrites.

The Hall effect and thermoelectric properties are widely used in the interpretation of the conduction mechanism in semiconductors. However, in the case of low mobility semiconductors such as ferrites, it is sometimes difficult to measure the Hall effect, in such cases the thermoelectric measurement technique is the only alternative. Moreover, the measurement of thermo-emf is simple and its sign gives vital information about the type of conduction in semiconductors.

The spinel ferrites containing Cu have shown interesting electrical, dielectric and magnetic properties [1]. The potential applications of Cu, Ni and Co based soft ferrites are well known, especially when these elements are partially substituted by zinc and cadmium. Furthermore,  $\text{Cu}^{+2}$  containing ferrites are

supposed to be a unique spinel because its cation distribution is variable and the presence of  $\text{Cu}^{+2}$  ions led to severe Jahn-Teller type distortion.

Several investigators have studied IR spectra and thermoelectric power of  $\text{Zn}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$  [2-3], d.c. conductivity and dielectric constant measurements as a function of temperature and frequency on  $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  system [4, 5]. Some works have been reported on studies of the thermoelectric power of  $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$  [6].

Detailed study on electrical properties of  $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$  [7], the effect of sintering temperature and frequency on the electrical properties of  $\text{Co}_{0.22}\text{Zn}_{0.78}\text{Fe}_2\text{O}_4$  ferrite [8] and dielectric behaviour and a.c. electrical conductivity of Zn - substituted Ni-Mg ferrites [9] have been carried out.

No systematic studies on the temperature and concentration dependence of electrical properties of  $\text{Zn}^{2+}$  substituted  $\text{CuFeCrO}_4$  system have been reported in the literature, except our earlier study on magnetic properties [10, 11] and the recent study on structural properties [12] of the  $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$  system. Hence, an attempt has been made to investigate the effect of substitution of  $\text{Zn}^{2+}$  on the thermal variation of electrical behaviour of  $\text{CuFeCrO}_4$  by means of resistivity and thermoelectric power measurements.

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## 2. Experimental details

The powdered samples of  $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$  have been prepared by usual double sintering ceramic method, with composition  $x = 0.0, 0.2, 0.4$ , and  $0.6$ . The details regarding sample preparation and X-ray diffractometry have been given in our earlier communications [10-12].

The samples for electrical measurements were in the form of disc 10 mm in diameter and 3 mm thick and both the faces of each disc sample were polished by rubbing with zero grade emery paper, washed in dilute HCl and acetone. Finally, graphite was rubbed on both flat faces of the samples on which aluminium foil was also kept for good electrical contacts.

The resistance of a pellet was measured by the two terminal pressure contact method using BPL made Meg-ohm meter. Thermal variation of resistance was obtained by placing sample holder containing a pellet in a horizontal electric furnace and temperature was measured by chromale-alumel thermo-couple. The resistance of the pellet was measured during the decrease of temperature at the step of  $10^\circ\text{C}$ .

Thermoelectric power studies were carried out over a temperature range 300-500K by the differential method. The temperature gradient was measured by two chromale-alumel thermo-couples which were kept very close to the sample while thermo-emf was measured with the help of a digital microvoltmeter with an accuracy of  $\pm 3\%$ .

In order to achieve good thermal stability, the values of the thermo-emf have been recorded while cooling. The sample is maintained at a given temperature for about 5-10 minutes.

## 3. Results and discussion

The compositional dependence of resistivity ( $\rho$ ) at 300K is represented in Table 1. The resistivity ( $\rho$ ) increases with increase in zinc-content( $x$ ). This happens because the replacement of  $\text{Cu}^{2+}$  by  $\text{Zn}^{2+}$  in  $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$  system dilutes conduction through the octahedral sites. The incorporation of  $\text{Zn}^{2+}$  ions which do not participate in the conduction process, limits the degree of  $\text{Fe}^{3+} + \text{Cu}^{2+} \rightarrow \text{Fe}^{4+} + \text{Cu}^{1+}$  and  $\text{Cu}^{1+} + \text{Cu}^{2+} \rightarrow \text{Cu}^{2+} + \text{Cu}^{1+}$  conduction that occurs. Thus, the efficient method of curtailing the conduction process is the replacement of the effective ion ( $\text{Cu}^{2+}$ - $\text{Cu}^{1+}$ ) by less effective ones ( $\text{Zn}^{2+}$ ).

**Table 1.** Resistivity ( $\rho$ ) and Neel temperature ( $T_N$ ) for Zn-Cu-Fe-Cr-O system

Content $x$	$\rho$ ( $\Omega\text{cm}$ )* $10^5$ (300K)	$T_N$ (K) Resi	$T_N$ (K) Susc [10]	$T_N$ (K) Theory[15]
0.0	0.95	571	575	575
0.2	1.00	512	510	498
0.4	62.3	416	420	418
0.6	815.1	349	350	310

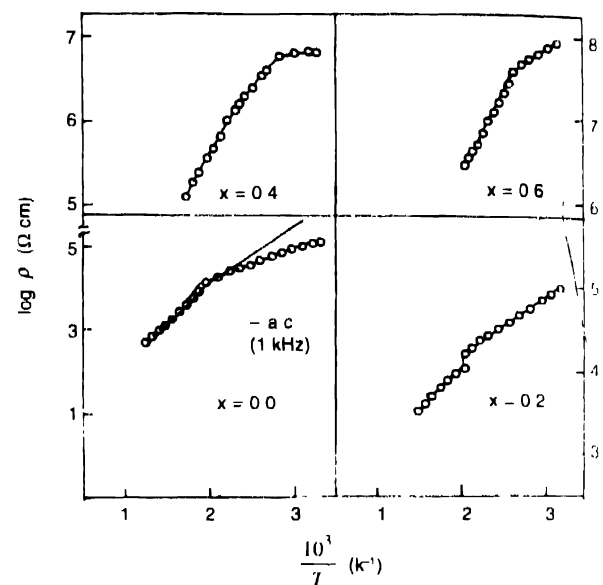
$T_N$  (K) Error  $\pm 5\text{K}$

Furthermore, the room temperature resistivity ( $\rho$ ) for all the samples was found to be of the order of  $10^5 \text{ ohm.cm}$ . (Table 1), indicating the absence of mixed valency in the samples.

The electrical resistivity as function of temperature ( $T$ ) for the system  $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$  in the form of Arrhenius plots of  $\log_{10} \rho$  versus  $10^3/T$  are shown in Figure 1 for all four compositions. The temperature dependence of resistivity is given by the Arrhenius equation.

$$\rho = \rho_0 \exp(\Delta E / kT), \quad (1)$$

where  $k$  is Boltzmann's constant,  $\Delta E$  is the activation energy and  $T$  is the absolute temperature.



**Figure 1.** Electrical resistivity versus temperature for  $x = 0.0, 0.2, 0.4$  and  $0.6$  samples

As shown in Figure 1, the curve consists of two straight line portions; hence there are two activation energies for the two different ranges. The reason for the two slopes can be explained as follows: At high temperature, the thermal energy is sufficiently great to create vacancies and the activation energies represents a sum of the energies required for vacancies generation and the motion of ions into the vacancies. At lower temperature, the thermal energy is only large enough to allow the migration of atoms into vacancies already present in the crystal. A change in the slope may be due to the Neel temperature [13] or to the change in the conductivity mechanism [14]. This anomaly strongly supports the influence of magnetic ordering upon the conduction process in ferrites.

The Neel temperature ( $T_N$ ) deduced for all four compositions from  $\log \rho$  versus  $10^3/T$  plots are listed in Table 1. It is found that the values of  $T_N$  are in good agreement to those found experimentally from a.c. susceptibility measurements [10] and those calculated theoretically using modified molecular field theory [15] (Table 1).

The activation energy values for conduction are computed from  $\log \rho$  versus  $10^3/T$  plots and the same are tabulated in Table 2. The activation energy increases on changing from ferrimagnetic ( $E_f$ ) to paramagnetic ( $E_p$ ) region. According to the theory of magnetic semiconductors, one expects a reduction in the activation energy as the system undergoes the transition from paramagnetic to ferrimagnetic state. Similar results have been observed for Cu-Cd [16], Cu-Ni [17], Cd-Ni-Ti-Fe [18], Cu-Cd-Gd-Fe [19] mixed ferrites systems. According to Rezlescu *et al* [20] the change  $\Delta E = E_p - E_f$  is associated with the ordering temperature roughly given by the relation  $\Delta E = AKT_N$ , where  $E_p$  and  $E_f$  are activation energies below and above  $T_N$ . The value of the proportionality constant  $A$  is found to be  $\sim 4.5$  for all compositions. The value 4.5 is in good agreement with that reported for Cu-Mn-Zn ferrites [20]. It is interesting to note that no considerable change in  $\Delta E$  is observed for present system (Table 2). According to Ahmed *et al* [21], if the substituted cations occupy  $B$ -sites then the effect on  $\Delta E$  is greater and Devalle *et al* [22] suggest that when the substitution is made on  $A$ -sites without disturbing  $B$ -sites, then almost no change in  $\Delta E$  is observed. The change in  $\Delta E$  with  $x$  for present system suggest that  $Zn^{2+}$  ions occupy  $A$ -sites with some sort of disturbance on cationic distribution on  $B$ -sites as confirmed by cation distribution formulae [10-11].

Table 2. Activation energy and Fermi energy for Zn-Cu-Fe-Cr-O system

Concentration $x$	$E_f$ (eV)	$E_p$ (eV)	$\Delta E$ (eV) $E_p - E_f$	$E_f(0)$ (eV)
0.0	0.188	0.418	0.230	0.03
0.2	0.142	0.384	0.242	0.16
0.4	0.191	0.357	0.166	0.16
0.6	0.177	0.316	0.139	0.03

For the sake of comparison variation of  $\rho$  resistivity (1 kHz) with temperature was carried out for typical sample  $x = 0.0$ . It was observed that the  $\rho_{ac}$  resistivity is slightly higher than  $\rho_{dc}$  resistivity within temperature range 300-450 K. It predicts that the electrical conductivity in this range is composed of two contributions viz. electronic and ionic. Higher values of  $\rho_{ac}$  as compared to  $\rho_{dc}$  suggest that some sort of impurities are present in the compounds due to which dielectric loss occurs. Above  $T \sim 450$  K,  $\rho_{ac}$  and  $\rho_{dc}$  resistivity coincide. It indicates that the concentration of the electronic charge carriers becomes much larger than the concentration of free ions. Hence, at the temperature above  $T \sim 450$  K, the electrical resistivity due to free ions become negligible and it is entirely electronic.

The Seebeck coefficient ( $\alpha$ ) is given by the relation :

$$\alpha = \Delta V / \Delta T \quad (2)$$

where  $\Delta V$  is the voltage measured across the sample and  $\Delta T$

the temperature difference across the sample. Figure 2 shows the temperature variation of thermo electric power ( $\alpha$ ) for  $Zn_xCu_{1-x}FeCrO_4$  system. The common feature for all the composition is that  $\alpha$  is negative over the whole range of temperature, indicating that the charge carriers are electrons. It is clear from Figure 2 that the magnitude of ' $\alpha$ ' is found to decrease continuously with increasing temperature for all the samples. The temperature dependence of ' $\alpha$ ' is mainly determined by the concentration of  $Fe^{3+}$  ions in the octahedral site and this may be attributed to the predominance of impurity conduction in this region. Therefore, conduction phenomenon in these ferrites is due to impurity conduction at lower temperatures while it is due to the polaron hopping at higher temperature. There is strong experimental evidence of the existence of polarons and their hopping process [23].

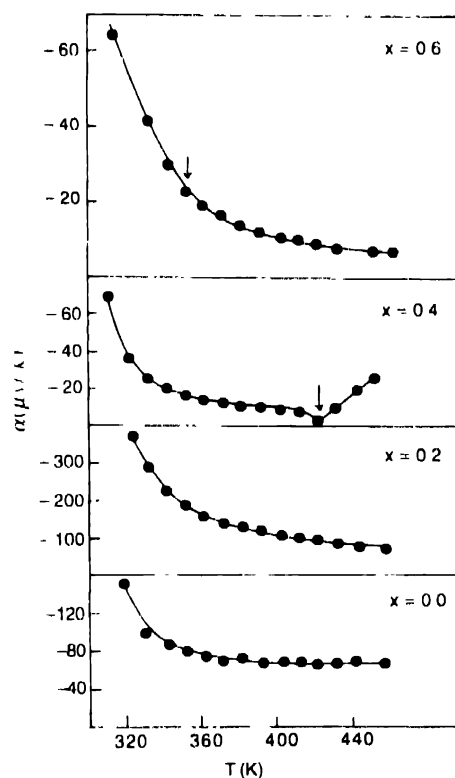


Figure 2. Variation of Seebeck coefficient with temperature for  $x = 0.0, 0.2, 0.4$  and  $0.6$  compositions

In the region where conduction is due to one kind of charge carriers, the relations between the Seebeck coefficient ( $\alpha$ ) and Fermi energy ( $E_f$ ) will be given by [24]

$$E_f = e\alpha T - AkT, \quad (3)$$

where  $A$  is a term connected with the kinetic energy of carriers,  $e$ ,  $k$  and  $T$  are electronic charge, Boltzmann constant and absolute temperature, respectively. The calculated values of  $E_f$  as a function of temperature for two values of  $A$  ( $A = 0$  and  $2$ ) are shown in Figure 3. The extrapolated value of  $E_f$  to  $T = 0$  K, yields the values of  $E_f(0)$  (Table 2).

Comparing the activation energies of ferrimagnetic region ( $E_f$ ) with  $E_f(0)$ , it is seen that  $E_f > E_f(0)$ . The difference between two values can be attributed to an activation energy associated with the drift mobility of electrons. Thus, the activation energy consists of one part associated with the generation of electrons and the other part associated with the hopping of the polarons between equivalent sites.

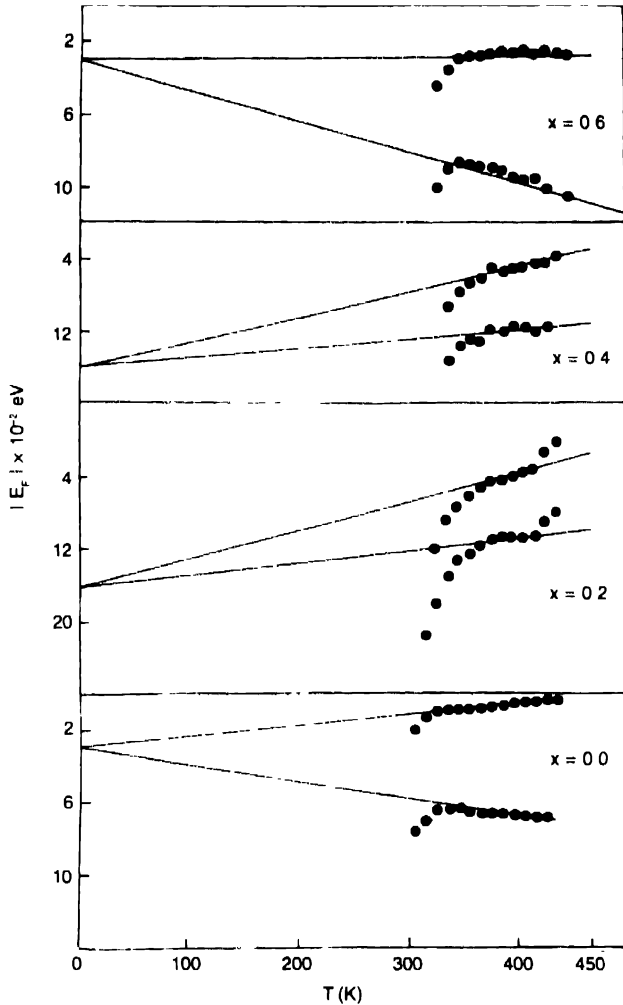


Figure 3. Thermal variation of fermi energy ( $E_f$ ) for  $x = 0.0, 0.2, 0.4$  and  $0.6$  samples

#### Charge carrier concentration ( $\eta_c$ ) and mobility ( $\mu_c$ )

From the values of  $\alpha$ , the values of carrier concentration ( $\eta_c$ ) have been calculated using the formula [25, 26]

$$\eta_c = N/V \left[ 1 / \{ 1 + \exp(-\alpha e/k) \} \right], \quad (4)$$

where  $N$  is the density of states (can be taken as  $10^{22} \text{ cm}^{-3}$  [27]),  $V$  is the volume of the sample under study and  $k$  the Boltzmann constant. It is found that  $\eta_c$  increases continuously with increase of temperature.

The charge carrier mobility ( $\mu_c$ ) has been calculated from the experimental values of conductivity ( $\sigma$ ) and those of

carriers concentration ( $\eta_c$ ) using the well known relation

$$\sigma = \eta_c e \mu_c \quad (\mu_c \gg \mu_h). \quad (5)$$

The values of mobility are found to be very low as compared to normal semiconductors. It was observed that initially the mobility decreases upto certain temperature ( $T < 350 \text{ K}$ ). However, beyond that temperature, ( $T > 350 \text{ K}$ ) the  $\mu_d$  increases continuously with increase of temperature.

#### Conduction mechanism :

The observed increase in mobility with increasing temperature suggests that :

The responsible mechanism for the conduction in  $\text{Zn}_{1-x}\text{Cu}_x\text{FeCrO}_4$  ferrites is hopping of charge carriers from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions on octahedral sites rather than the band mechanism

The charge carriers responsible for the conduction process may be small polarons rather than electrons. In solids with large coupling constant and narrow conduction band, small polaron formation is more probable [28]. In oxides of iron group metals the overlap of  $3d$  wave functions between the neighboring metal ions is relatively small. Based on the experimental evidence of existence of small polarons and hopping process, it can be concluded that the conduction in  $\text{Zn}_{1-x}\text{Cu}_x\text{FeCrO}_4$  mixed ferrites at high temperatures may proceed via thermally activated hopping motion of strongly correlated polarons. On the other hand at lower temperatures, the weakly activated hopping motion of polarons might degenerate in Brownian like motion resulting in tunneling instead of hopping of polarons.

On examining the variation of  $\eta_c$  and  $\mu_d$  as a function of temperature, it is evident that the change in charge carrier mobility ( $\mu_d$ ) is greater than that in carrier mobility ( $\eta_c$ ) for a given temperature difference indicating that the increase of conductivity (or decrease of resistivity (Figure 1)) is essentially influenced by the mobility rather than the carrier concentration. This could be due to the fact that the charge carriers are localized at ions or vacant sites. Due to the lattice vibrations, the ions occasionally come close enough for the transfer of charge carriers and the conduction is therefore induced by lattice vibrations, and as a result the carrier mobility shows an exponential temperature dependence with an activation energy.

#### 4. Conclusions

The results obtained from various electrical properties of  $\text{Zn}_{1-x}\text{Cu}_x\text{FeCrO}_4$ , it is concluded that ;

- (i) The change in slope in resistivity versus temperature curve near Neel temperature, strongly supports the influence of magnetic ordering upon the conduction process in ferrites.
- (ii) All the samples are  $n$ -type semiconductors and the electrical conduction in this materials take place by two distinct conduction mechanism below and above  $450 \text{ K}$ .

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